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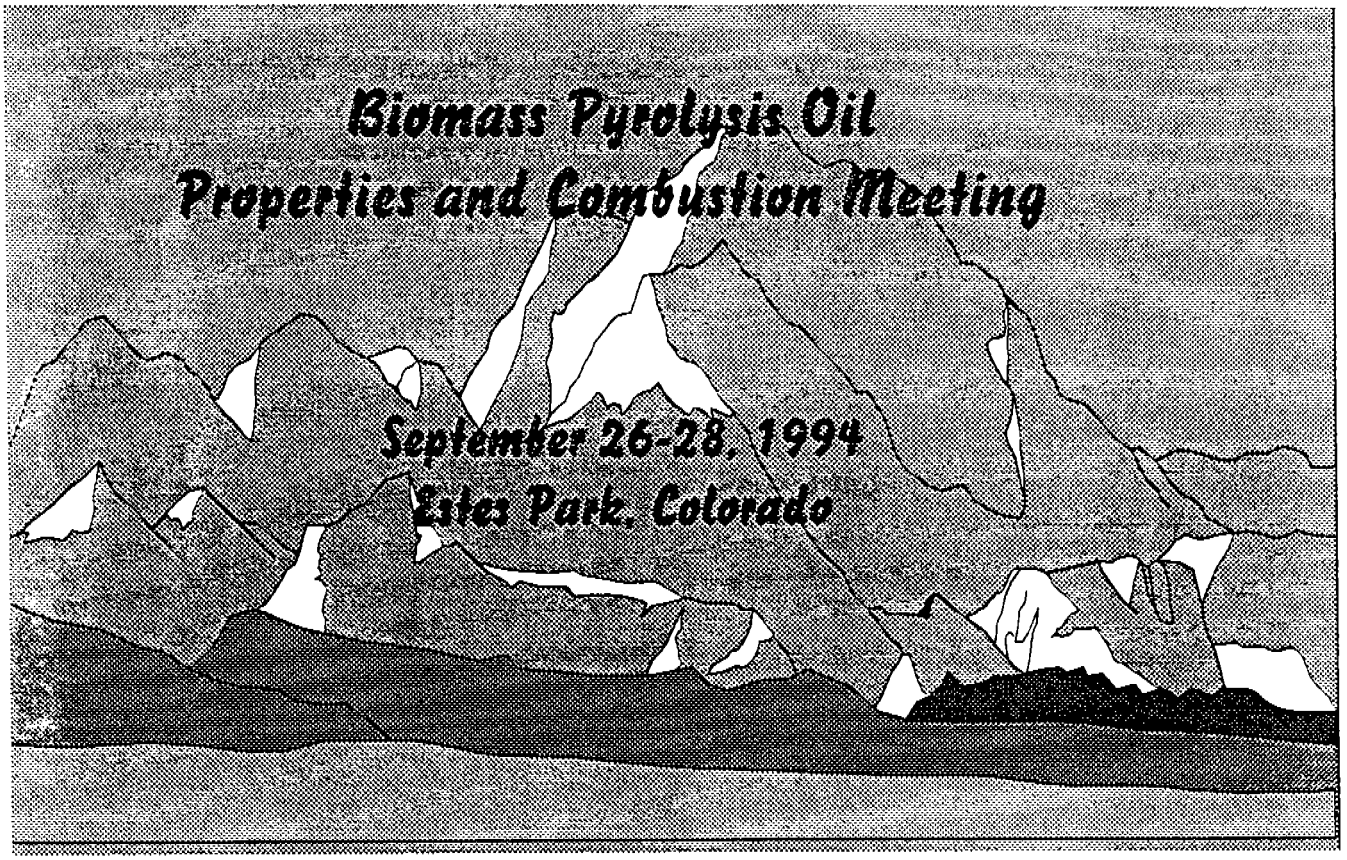

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INORGANIC COMPOUNDS IN BIOMASS FEEDSTOCKS: THEIR ROLE IN CHAR FORMATION AND EFFECT ON THE QUALITY OF FAST PYROLYSIS OILS

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Abstract

Inorganic compounds especially potassium, calcium, sodium, silicon, phosphorus, and chlorine are the main constituents of the ash in biomass feedstocks. The concentrations of ash in biomass feedstocks range from less than 1% in softwoods to 15% in herbaceous biomass and agricultural residues. During biomass pyrolysis, these inorganics especially potassium and calcium, catalyze biomass decomposition and char formation reactions. Decomposition reactions may either result in levoglucosan-rich or hydroxyacetaldehyde-rich pyrolysis products depending on the concentration of the ash in the feedstocks. The catalytic effect of the ash levels off above 1.5% concentration. Chars formed during these reactions invariably end up in the pyrolysis oils. A high proportion of the alkali metals in the ash are sequestered in the chars and are suspended in the pyrolysis oils as submicron particles. These submicron char particles tend to agglomerate under cold storage conditions. The presence of high concentrations of alkali metals in the biomass pyrolysis oils makes them unsuitable for combustion in boilers and in turbine operations. The highest concentration of alkali metals are found in herbaceous feedstocks and agricultural residue pyrolysis oils.

Sequential cold filtration of the oils using filters of varying size revealed that most of the alkali metals detected in the pyrolysis oils are indeed trapped in the chars. Leaching studies conducted on the chars suspended in the oils showed no leaching of alkali metals from the chars into the oils. The alkali metals in the oil therefore originate from the suspended submicron char particulates. Our data suggest that hot gas filtration of the oils can effectively reduce the alkali metal contents of the pyrolysis oils to acceptable levels to be used as turbine and boiler fuels.

Introduction

The potential of biomass pyrolysis oils (biocrude) for large scale power production is attractive because of the hauling cost associated with the use of solid biomass, easier handling, distribution, and storage of liquid fuels. Additionally, biocrude is a potential feedstock for chemicals, it is highly oxygenated, and above all, it is a renewable resource. If biomass feedstock production is managed sustainably, the use of biocrude for power

generation will have no net contribution to the atmospheric carbon dioxide because the carbon dioxide produced during the combustion process would be captured by the plants during their growth. However, biocrude like any other fuel in their developmental stage, is plagued with several unique problems that have to be solved before it can have any significant impact on fuel supply. Some of the common problems associated with biocrude are: high acidity, high viscosity, instability during storage, high corrosiveness, high water content, alkali, and alkaline earth metal contents.

The alkali and alkaline earth metals content (especially potassium, sodium, and calcium) is the focus of this paper. The presence of these metals in biocrude have been projected as potential sources of fouling, corrosion, and erosion of turbine blades in power generation systems as well as fouling of steam boilers. This projection stems from the stringent specification of alkali metal contents in turbine fuels derived from petroleum resources. Because of the high sulfur contents of petroleum-derived turbine fuels, the presence of more than 1 ppm of alkali metals in these oils is unacceptable. It has been shown that the alkali metals form sulfates with sulfur oxides produced during combustion and these sulfates are principal sources of hot corrosion. Because the sulfur content of petroleum derived fuels cannot be reduced through distillation, there is a stringent requirement to lower the potassium and sodium contents of these fuels [1].

Gas turbine operators have shown that slag-forming compounds in oils can cause corrosion and deposit . Corrosion can result from vanadium, potassium, sodium and lead. These elements in addition to calcium can form deposits which are very difficult to remove from turbine blades [1]. Operation of biomass-fired turbines have also shown that, if gas inlet temperatures are less that 800°C, ash deposits on the turbine blades, which are extremely difficult to remove [2].

Pyrolysis oils produced from various biomass feedstocks which use fast pyrolysis processes are known to contain very high levels of alkali and calcium metal salts but those produced by vacuum pyrolysis have relatively low alkali and calcium contents [3]. However, the mechanism of inorganic material deposition in pyrolysis oils is not known. In this paper we discuss the probable mechanism of alkali metal deposition in the pyrolysis oils and in a companion paper to be presented at this workshop, some of the proposed methods of alkali metal removal are discussed [4].

Experimental

Pyrolysis Molecular Beam Mass Spectrometric Analysis (Py-MBMS).

Biomass feedstocks used in this study consisted of tall fescue (*Festuca arundinacea* Schreb.), alfalfa-orchardgrass (*Medicago sativa* L.-*Dactylis glomerata* L.), and switchgrass (*Panicum virgatum* L.) with different ash contents because of biological degradation. The biomass feedstocks were ground to 40 mesh and weighed in triplicates in quartz (20-

30 mg) and pyrolyzed at 500 °C in a hot helium atmosphere for 1.5 seconds. The pyrolysis was monitored by a molecular beam mass spectrometer (MBMS). The residue after the pyrolysis was cooled in helium gas at STP and weighed. The moisture content of the feedstock used for these studies was 5.6-6.2%.

Fluidized Bed Pyrolysis of Biomass Feedstocks.

To study the origin of alkali metals, calcium, and other trace inorganics content of biocrude, switchgrass (*Panicum virgatum* L.) was pyrolyzed in a fluidized bed reactor. Detailed description of the fluidized bed reactor has been published elsewhere [5]. The switchgrass samples were milled in a Wiley mill (model 4) to a Sauter mean diameter of 345-400 μm. The pyrolysis temperature of the fluidized sand bed was 500 °C and the fluidizing gas was nitrogen. The pyrolysis vapor residence time in the free volume of the reactor was <0.4 s. Pyrolysis vapors were condensed in a condensation train which consisted of chilled water condenser, ice/salt condenser, electrostatic precipitator, and a cotton wool trap. The oils from the condensers were recovered by washing with acetone. The acetone washed oils were made up to a total volume of 5 L and samples of 200 mL x 3 were taken from the unfiltered oil. The oils were then filtered sequentially through a 40-60 μm, 10-15 μm, 4.0-5.5 μm, 1.0 μm, and 0.7 μm filters. During each filtration stage, 200 mL x 3 samples were taken. The acetone soluble oils were recovered by rotary vacuum evaporation (18 mm Hg and 40 °C). The samples were sent to Huffman Laboratory, Golden, Colorado for ash, potassium, sodium, calcium, silicon, chlorine, and phosphorus analysis.

A second set of samples was prepared by filtering acetone soluble oils through a 40-60 μm filter and storing a 5 L sample in a cold room (10 °C) for 1, 2, 7, 15, and 30 days. At the end of each storage period, 200 x 3 mL samples were taken and filtered through a 10-15 μm filter. The oil was recovered by vacuum evaporation as above. These samples were also analyzed by the same laboratory for the same elements as above.

Results and Discussion

Pyrolysis Molecular Beam Mass Spectrometric (Py-MBMS) Analysis

The herbaceous feedstocks used in this study were switchgrass, tall fescue and alfalfa-orchardgrass. Ash contents of these feedstocks ranged from 4 - 12% which were very high compared to woody biomass feedstocks. Part of the high ash content can be attributed to unprotected outside storage of the feedstock for a 9 month period duration. This outside storage resulted in both partial microbial degradation and weathering of the feedstocks, hence the ash contents increased very significantly and a wide variation of ash contents were observed for various samples.

In Figure 1, the char yields on moisture-free ash-free basis are plotted against the

potassium and calcium contents of the feedstocks. The influence of calcium and potassium contents of the feedstocks on char formation appears to be non-linear. At low inorganic concentrations in the feedstock, the catalytic effect appears to be more vigorous than at higher concentrations as shown by the steeper slope of the curve. At high potassium and calcium concentrations, the yield of char levels off under our pyrolysis conditions.
The above data suggest that there are at least two mechanisms of char formation: one initiated by inorganic constituents of the biomass and the other by condensation reactions of the pyrolysis products.

The char data suggests that activity of the inorganic materials is dependent on the number of active sites available in the biomass and char formation reactions are initiated from these sites only. Once the active sites are saturated, it appears the excess potassium and calcium present do not take part in the reaction. DeGroot et al [6] reported increase in char formation when inorganic salts were added beyond the exchange capacity of cottonwood, but they did not go beyond 2% of inorganics and thus they did not observe the levelling off effects observed in our study. However, they reported that the incremental effects of char yield was less as the ash level increased, which agrees with our data. They speculated that the sites available for ion-exchange of inorganic species is dictated by the amount of hemicelluloses present in the biomass feedstock. It has also been observed that the catalytic effect of inorganic species on the conversion of cellulose to hydroxyacetaldehyde appears to be non-linear and drops off with increasing amounts of inorganic ions [7, 8]. This again shows that the catalytic activity of the inorganic ions are directed by the number of active sites available, probably the number of uronic acid sites which bind the inorganic compounds. The potassium and calcium catalytic activity also appears to be mass transfer limited, because the inorganics appear to be the center of reaction and char formed during the pyrolysis reaction covers the surface of the particles. As the reaction proceeds, char builds up on the surface of the catalyst particle and slows down the reaction until it eventually stops. Thus char particles formed by this process will have a high concentration of inorganics in the center of the particle. This is illustrated by the high concentration of the inorganic material in the chars obtained from the fluidized bed pyrolysis of switchgrass described in the next section. However, the exact mechanism of the char formation is not understood. We did not investigate the effect of other inorganic materials present in the biomass feedstocks on char formation reactions, so that the levelling off observed in these data could have been influenced by the presence of other inorganic compounds in the biomass.

The Role of Char in Biomass Pyrolysis Oils.

We have shown above that the inorganic constituents of biomass feedstocks play some role in the formation of char during pyrolytic reactions. In the fluidized bed pyrolysis process, some of the char formed during the pyrolysis process is suspended in the fluidization gas and transported out of the reactor. A cyclone separator installed in the pyrolysis train captures over 90% of the char carried over by the fluidization gas, but char

particles below 10 μm normally escape from the cyclone and condense with the oil.

Table 2 shows the reaction conditions and the material balances for the fluidized bed pyrolysis runs of switchgrass feedstock. Total liquid yields were relatively low compared to pyrolysis of woody feedstocks under similar conditions. The char content of the pyrolysis oil after filtration through 40-60 and 10-15 μm was 2-3%. Smaller filter sizes did not produce any significant amounts of char. The ash contents of the chars recovered from the pyrolysis oils ranged from 9-15% while ash contents of the filtered oils were very low (<0.05%) except for the unfiltered oil that had ash content of 0.45%. The ash content of the chars was more than double that for the feedstock (Table 1). The high ash content of the chars suggests that a large fraction of the inorganic species was sequestered in the char fraction. This observation was confirmed by the high concentrations of the potassium and other elements in the char and low concentration of these elements in the pyrolysis oil (Table 3 and 4).

Although the ash content of the pyrolysis oil was very low (<0.05 to 0.49%), the potassium and calcium levels were prohibitively high for application as turbine fuel. The concentration of potassium in these oils range from 160 - 300 ppm, and those for calcium ranged from 1-95 ppm whereas turbine fuel specification requires total alkali metals content of 1 ppm. Concentrations of other inorganic elements in the pyrolysis oils were equally high (Table 3).

Sequential filtration of the condensed pyrolysis oils dissolved in acetone revealed some interesting results. The raw unfiltered oil as expected had the highest potassium and calcium contents but the contents of these metals decreased gradually as the raw oil was filtered sequentially through different filter sizes. The concentration of potassium and calcium finally levelled off at around 4-5.5 μm (see Figure 2). This concentration trend was similar for silicon and phosphorus in the oils. For chlorine and sodium, the data was very scattered and no concrete conclusion could be drawn on the effect of filtration of the oil on element distribution in the oil.

The gradual decrease in the potassium and calcium contents of the oil with the decrease in the filter size clearly suggests that fine char particles in the oils were partly responsible for the high concentration of these elements in the oils. Furthermore, oils from vacuum pyrolysis process which do not use fluidizing gas or entrainment gas as in the ablative pyrolysis (vortex reactor) process have been shown to contain very low concentrations of both char and alkali metals [3]. However, because the potassium and calcium contents of the oil did not extrapolate to zero (Figure 2), this also suggests that some of the inorganic material may reside in the oil phase or that there are submicron char particles which escaped the smallest filter (0.7 μm). Alkali metals and other inorganics may get into the oil phase by the following mechanisms: leaching of inorganics from the char into the oil phase; vaporizing of the inorganics during the pyrolysis run and condensation with the oils or a combination of both. Our thermodynamic calculations show that the vaporization mechanism plays a minimal role in the transport of potassium, sodium, and

calcium into the oil phase. At 500 °C, most potassium, sodium, and calcium salts have very low vapor pressure and therefore are not likely to contribute significantly to the inorganics in the oil phase. Thus the only credible source of transportation of alkali into the oil phase is through leaching of the inorganics sequestered in the submicron char that escaped capture by the cyclone separator.

The biomass pyrolysis oils have very low pH (2-3) because of the formic and acetic acids as well as glyoxal and other acidic compounds in the oil. Under these acidic conditions, it is possible that the inorganics could leach into the oil. The rate of mass transfer will depend on the concentration of the inorganic species, the char particle size, and the porosity of the particle.

Leaching of inorganics of pyrolysis chars

To ascertain whether leaching is the sole mechanism of mass transport of inorganics (especially) potassium into the oil phase, oil leaching studies were carried out. The data (Figure 3) show that within the limits of experimental error, the potassium content of the oil decreases with storage time. This result was very surprising to us because it suggests that, even under the highly acidic oil environment, there was no leaching of potassium from the char into the oil phase under the cold room conditions. Instead, it appears that there was agglomeration of the submicron char particles in the oils. These agglomerated submicron particles were large enough to be removed during the filtration stage and this resulted in the decrease in the potassium content of the oil during storage. However, this phenomenon equilibrates within seven days of storage of the oil samples and no further decreases were observed after 30 days od cold room storage. Similar trends in the concentration of other inorganic elements in the char were observed. It should be pointed out that studies at other higher temperatures could indicate otherwise because leaching rates are generally higher at higher temperatures.

Thus, it appears that alkali metals exist in the pyrolysis oils as sequestered suspension of submicron char particulates which do not leach into the oil phase under cold storage conditions. If the char particles could be removed from the pyrolysis vapors before they condense with the oils, or if a nanofiltration technique could be applied to the oils, then the alkali metal contents could be reduced to perhaps acceptable levels for use as turbine fuel. Preliminary hot gas filtration studies have indicated that the alkali metal content of the pyrolysis oils could be reduced to below 10 ppm, but at the expense of cracking some of the pyrolysis oils because of longer residence time in the hot filter.

Trace Inorganic Analysis

The analysis of trace inorganics in biomass pyrolysis oils appears to be a challenging task. According the local commercial laboratories in Colorado, the ashing of the oils using ASTM methods appears to be the most suspect of all the procedures. A graphitic type of carbon appears to be formed during the ashing process and this makes the ashing very

difficult. Furthermore, the atomic absorption method is limited to 10 ppm detection limit with a precision of ±10%. The heterogeneity of the oils make microsampling very difficult. The plots in Figures 2 and 3 clearly illustrate this point. The largest error bars are shown for the oil samples with the largest char concentration (unfiltered oil), but as the oil is filtered, the samples become more homogeneous and hence the error bars on the potassium and calcium determinations decrease. In a detailed discussion of this topic, Diebold et. al. [4] have shown that neutron activation analysis may be a better method of analysis for these oils.

Table 1. Composition of switchgrass feedstock

Element	Composition
Carbon (%)	45.1
Hydrogen (%)	6.1
Oxygen (%)	42.8
Nitrogen (%)	0.56
Chlorine (%)	0.68
Ash (%)	4.92
Calcium (ppm)	2400
Potassium (ppm)	8500
Sodium (ppm)	31
Phosphorus (ppm)	850
MJ/kg	

Table 2. Product yields and material balance for the fluidized bed pyrolysis of switchgrass feedstock.

	Run#1	Run#2
Pyrolysis Temp (C)	500	500
Char Yield (%)	18.8	19.0
Total Liquid Yield (%)	60.2	63.1
Gas Yield (%)	13.6	12.6
Mass Closure (%)	92.6	94.7

Table 3. Trace inorganic analysis of switchgrass pyrolysis oils. (The errors are standard deviations on 3 determinations).

Filter size (μm)	K (ppm)	Na (ppm)	Ca (ppm)	Si (ppm)	P (ppm)	Cl (%)	Ash (%)
Unfiltered	319±55	8.0±1.4	95±23	8.0±1.8	52±13	0.16±0.01	0.45±0.16
40-60	273±3	8.1±0.5	11±0.7	7.7±0.5	5.9±0.4	0.22±0.06	0.15±0.05
10-15	212±9	10.2±0.7	1.1±0.2	1.6±0.1	0.5±0	0.16±0.04	<0.05
4-5.5	163±6	13.5±1.4	0.7±0.1	1.3±0.5	0.4±	0.14±0.04	<0.05
1.0	177±5	16.1±0.5	1.5±0.2	2.0±0.2	0.5±0	0.12±0.01	<0.05
0.7	175±10	16.6±1.8	2.2±0.7	1.4±0.3	0.6±0.1	0.16±0.03	<0.05

Table 4. Trace inorganic analysis of chars recovered from the pyrolysis of switchgrass feedstock.

Source of Char	K (ppm)	Na (ppm)	Ca (ppm)	P (ppm)	Cl (%)	Ash (%)
Run #1 40-60 μm filter	7700	225	5600	2700	1.02	9.5
Run #1 10-15 μm filter	8500	690	7100	3600	1.06	15.3
Run #1 Char pot	24000	155	7300	2700	na	na

Conclusions

Inorganic materials (especially potassium and calcium) in biomass feedstocks catalyze pyrolysis reactions and are sequestered in the char. The potassium and calcium catalytic activity appears to be mass transfer limited, because the inorganics appear to be the center of reaction and char formed during the pyrolysis reaction covers the surface of the particles. These inorganic particles which are covered with carbonaceous char are mostly responsible for the alkali metals in the oils. Their contribution to alkali metals in the oils is through suspension of the macro and submicron particles in the oils.

There appears to be no leaching of alkali metals from the char particles into the oil phase under cold storage conditions. Because of the submicron nature of the alkali metal-laden char particles, reduction of alkali metals in the oils cannot be easily accomplished through the filtration of the condensed oils. The best approach for the reduction of the alkali metals and other inorganics in the oils will be the removal of the char particles from the pyrolysis vapors by hot gas filtration or nanofiltration of the condensed oils.

Agglomeration of the alkali metal-laden submicron char particles in the oil takes place during cold room storage and this may cause problems for long term storage, transportation, and utilization of biomass pyrolysis oils.

The heterogeneity introduced into the oils by the submicron char particles also introduces significant errors in microanalysis of trace metals in the oils. There is a need for the development of improved methods of biomass oil analysis.

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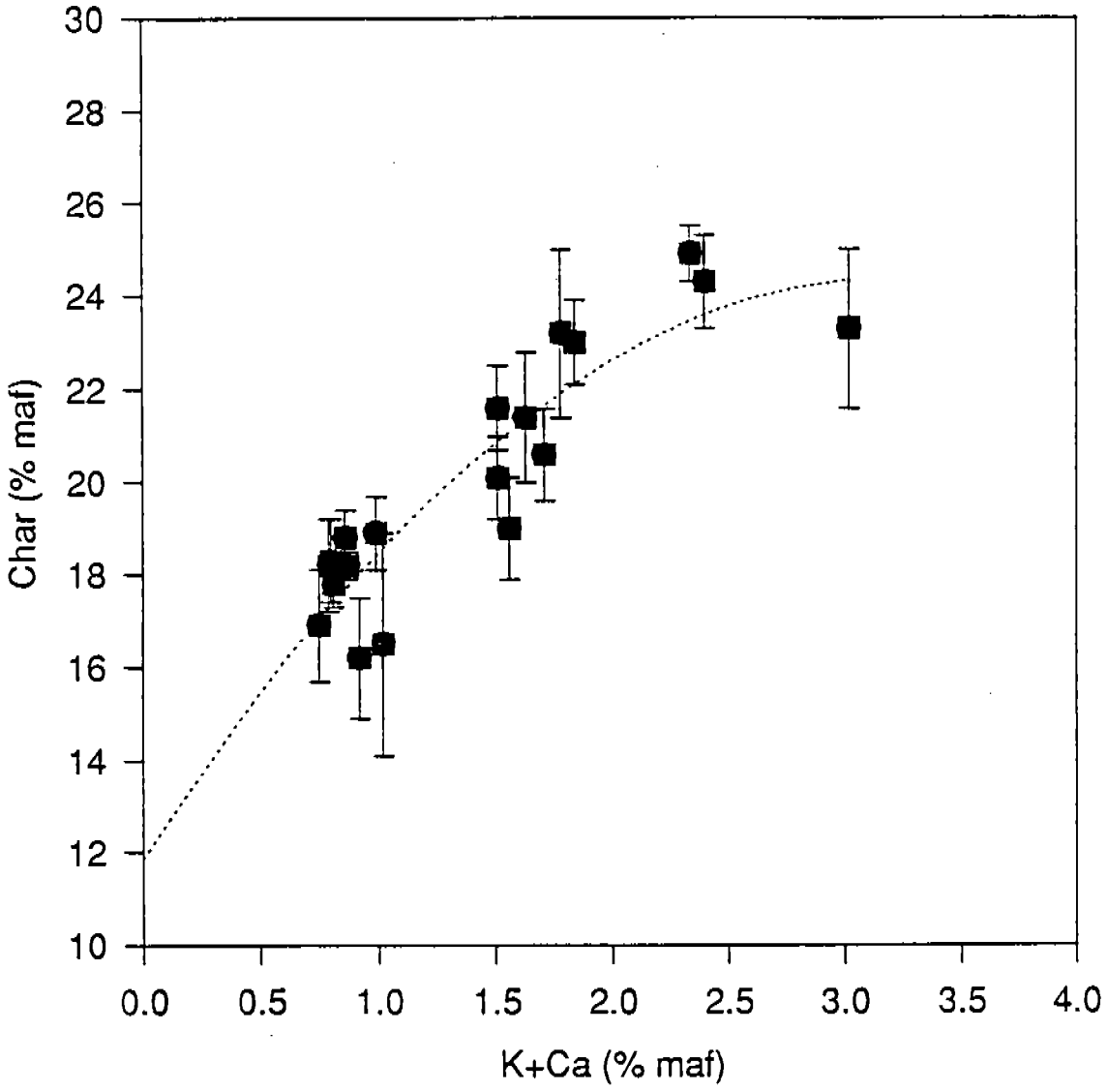

Figure 1. Influence of potassium and calcium contents of biomass feedstocks on formation at 600 °C.

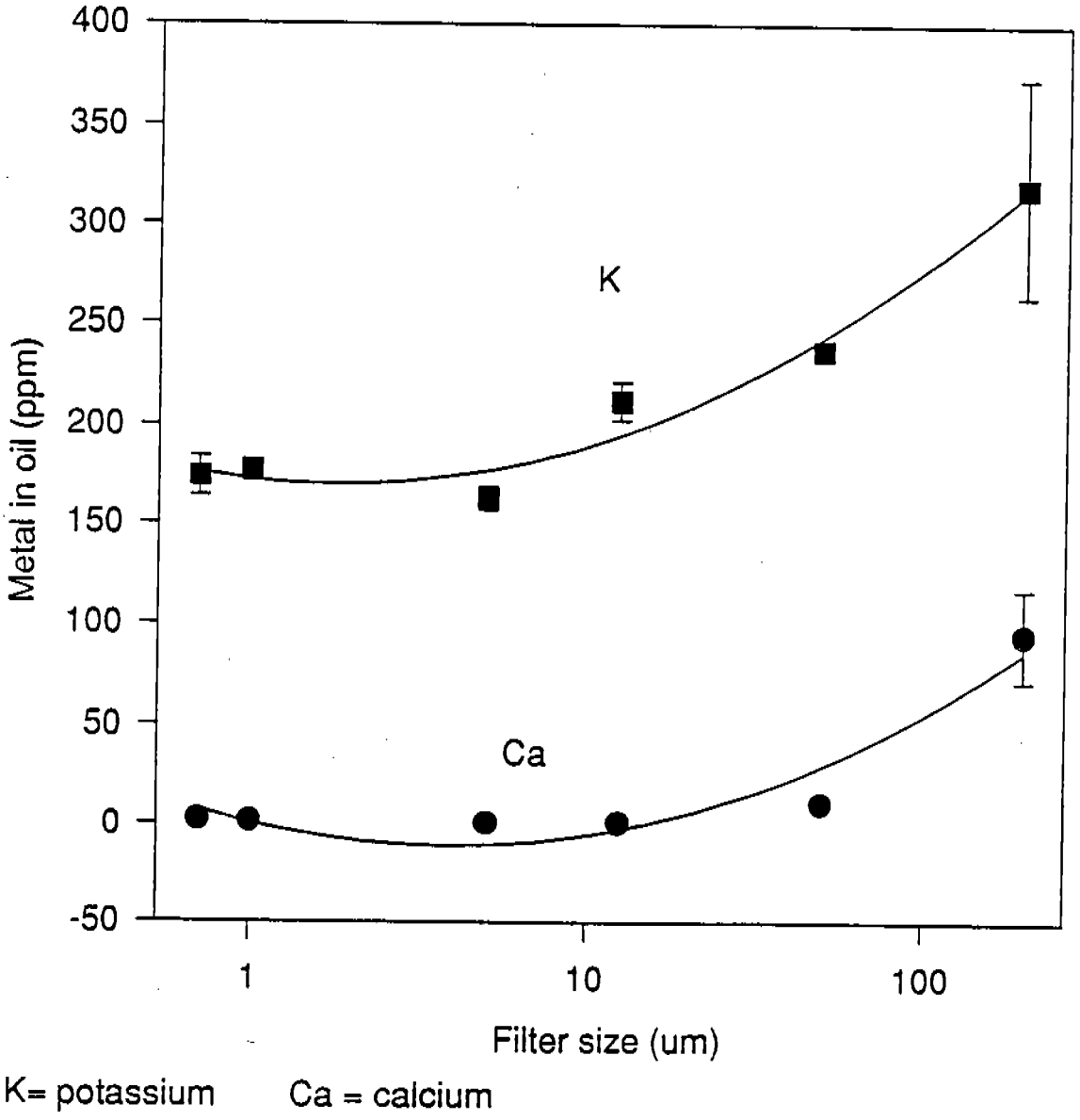

Figure 2. The effect of char on potassium and calcium contents of switchgrass pyrolysis oil. The oil was filtered through successive filters of decreasing pore size.

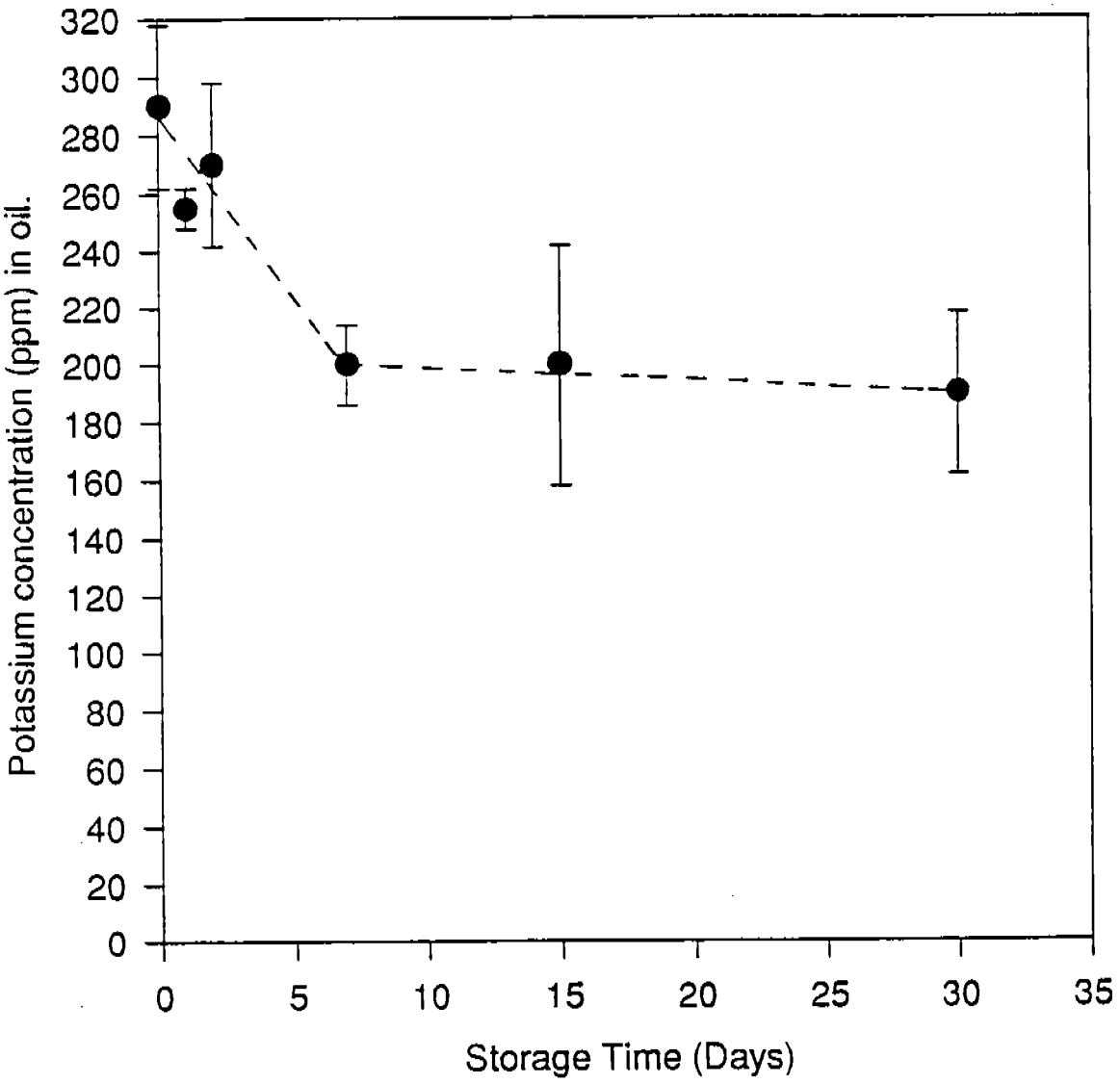

Figure 3. The influence of cold room storage on the potassium content of switchgrass pyrolysis oil. All oil samples were filtered through 10-15 μm filter before the potassium analysis.

HOT-GAS FILTRATION TO REMOVE CHAR FROM PYROLYSIS VAPORS PRODUCED IN THE VORTEX REACTOR AT NREL[1]

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ABSTRACT

The absence of char in pyrolysis condensates is required for them to be considered to have value above that of a residual fuel oil because of the alkali content of the char. During pyrolysis, the alkali-containing ash is concentrated in the char. This paper discusses hot-gas filtration of pyrolysis vapors produced in a vortex reactor at temperatures above the apparent dew point of the vapors prior to condensation.

A customized baghouse was commercially fabricated which has four filters and the ability to backflush each bag individually with a pulse of compressed gas. The size of the compressed gas pulse has been small enough to allow backflushing to occur during pyrolysis operations without shutting down. The nominal gaseous residence time of this design is on the order of three to five seconds. This baghouse is relatively unique in its capability to use either flexible, woven NEXTEL ceramic bags made by 3M or rigid sintered stainless steel filters made by MEMTEC. Based on samples of char made in the vortex reactor and collected with a cyclonic separator, the baghouse manufacturer projected a collection efficiency of 99.9%.

The cyclonic separator was removed from the vortex reactor system at NREL and replaced with the baghouse. A series of runs were made to evaluate this char separation technique to filter the total pyrolysis stream produced by the vortex reactor. The tendency of the pyrolysis oils to crack to permanent gases under these conditions is discussed as a function of operating temperature of the baghouse, based on previously determined kinetics.

Removing the char from the pyrolysis gas stream was demonstrated to be superior to that previously obtained using a cyclonic separator, based on the oil changing color from black to brown, lower ash content, and lower alkali metal content. In the case of switchgrass, the alkali metal content of the oil was lowered by two orders of magnitude. At the low alkali metal content of these oils, the analytical technique has not been very reproducible and has been under development. Heterogeneity of the oils has been blamed for the lack of reproducibility of the analysis for the several parts per million of alkali present.

BACKGROUND ON CHAR REMOVAL FROM PYROLYSIS OIL

Three products are formed during the pyrolysis of organic material: solid residue or char; permanent gases; and condensible vapors (organics and steam). Depending on the design of the pyrolysis reactor, the char is typically much smaller in size than the feedstock. With the vortex reactor, the char produced is a free-flowing powder. The mineral matter in the feedstock becomes concentrated in the char, giving the potential for mineral-free gases and condensible vapors if the char can be completely separated from the other products. In producing pyrolytic liquids from biomass and solid waste materials (e.g., short rotation woody crops, herbaceous crops, waste wood, municipal solid waste, etc.), a primary goal is to have a product that contains a minimum amount of suspended solids.

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[1]This paper was presented at the Specialists' Workshop on Biomass Oil Properties and Combustion, Estes Park, CO, Sept. 26-28, 1994.